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**14. ABSTRACT**

Report developed under STTR contract for topic AF08-T004. This report describes a Phase I feasibility study of applying a non-contact method for measuring creep in ultra high temperature ceramics. Low-precision samples were successfully processed at relevant temperatures, and coupled well to the new magnetic device used to induce the rotation that applies the load to the samples. Simulations based on published conventional measurements at lower temperatures indicate that the measurements are feasible for temperatures exceeding 1800 C for zirconium diboride and 1500 C for a composite of zirconium diboride with 25 volume percent silicon carbide at rotation rates that are within the design envelope for the apparatus. High-precision spheres were successfully manufactured from both materials. Delays in manufacturing prevented integrated trials with the high-precision spheres, however. Nevertheless, the combination of successful processing of low-precision spheres and promising results from the finite element simulations indicate that the method is feasible for measuring the creep of these ultra high temperature materials.

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TABLE OF CONTENTS



LIST OF FIGURES

## LIST OF TABLES



## GLOSSARY

| | |
|---|---|
| ESL | Electrostatic Levitation |
| ITI | Industrial Tectonics, Inc. |
| MSFC | NASA George C. Marshall Space Flight Center |
| NASA | National Aeronautics and Space Administration |
| NSWCCD | Naval Surface Warfare Center, Carderock Division |
| ppm | Parts per million |
| RHA | R. Hyers and Associates |
| UHTC | Ultra-High Temperature Ceramic |

## 1. IDENTIFICATION AND SIGNIFICANCE OF THE PROBLEM OR OPPORTUNITY

Speed can be a critical advantage to the warfighter. High-speed propulsion technologies enable the capability to defeat a time-critical target, to escape a threat, and to provide rapid reconnaissance and responsive access to space. [1,2]. Rockets provide very high speeds, but with limited specific impulse, which is the duration of thrust per mass of propellant. One limiting factor in rocket performance is time-dependent deformation (creep) in the throat of the nozzle, especially in solid rockets with non-eroding throats. On the other hand, hypersonic aircraft powered by scramjets can achieve much higher specific impulse, allowing flight durations of minutes to hours at speeds in excess of Mach 8. However, the performance of these hypersonic vehicles is limited by the capability of the vehicle to resist the aerodynamic heating, particularly on the leading edges of the wings and engine inlet.

Both non-eroding rocket nozzles and sharp leading edges for hypersonic vehicles require materials that will survive service conditions over 2200°C for minutes to hours. Meeting these needs will require significant improvements in our fundamental understanding of the response of materials at such high temperatures, especially their resistance to creep. However, conventional methods for measuring creep of these materials have severe limitations that often restrict designers to extrapolating properties from lower-temperature tests.

Research on ultra-high temperature ceramic (UHTC) materials has been performed only sporadically over the last 30 years, resulting in "a scarcity of fundamental research data available on the mechanical performance and manufacturability of UHTCs" [3]. One key factor limiting the maturation of these materials is our inability to measure their performance under the loads and at the extreme temperatures to which they are exposed in service. Our team has demonstrated a new method for measuring creep at up to 2300°C [4]. The method is readily extensible to over 3400°C [5]. The method has been demonstrated at stresses exceeding 10 MPa, with higher load capability under separate development.

Making this method commercially available for standardized testing of UHTC's will accelerate both basic research and the development of new materials required for providing greatly enhanced capabilities to the warfighter.

## 2. REVIEW OF PHASE I TECHNICAL OBJECTIVES

For $100,000 and 9 months, we proposed to demonstrate the capability of our method to measure creep of UHTC's at temperatures exceeding 2200°C, using small inexpensive samples and a non-contact design. Demonstration tests were to be conducted on at least two materials. The materials selected were pure $ZrB_2$ and a $ZrB_2$ composite with 25 volume % SiC. The samples were consolidated from 10 μm $ZrB_2$ powder and 2 μm SiC powder by the Naval Surface Warfare Center, Carderock Division (NSWCCD), as described by Talmy, *et al.*, [6].

This objective was divided into certain research questions: Can high-precision UHTC spheres be processed in Electrostatic Levitation (ESL) at the relevant temperatures and for the required duration? Can ESL provide sufficient stress to get the desired strain rates? Can the demonstrated methods for data collection, reduction, and analysis be adapted to the measurement of UHTC's? How do the results compare to extrapolations from lower-temperature conventional tests?

Proposed tasks:

1. Process UHTC materials at the relevant temperatures in Electrostatic Levitation for extended periods.
2. Prepare the required high-precision spheres from UHTC materials.
3. Apply sufficient rotation in the sample to cause creep.
4. Measure the creep deformation to sufficient precision and accuracy to allow analysis.
5. Extract the constants in the creep constitutive equation.
6. Compare results to the values reported in the literature and report.

## 3. PHASE I WORK: METHODS, RESULTS, AND DISCUSSION

### 3.1 Background on conventional creep methods

Conventional equipment for measuring creep uses tensile or/and compressive loads applied to samples heated by an electric or induction furnace. The upper end of a specimen is gripped by a fixture and a weight is attached at the lower end to apply a constant load. Fixtures are in contact with the specimen, therefore, they must be made of the materials which have equal or better chemical and mechanical stability than the specimen at high temperatures. At high temperatures, the specimen becomes more reactive, such that it may be incompatible with the testing apparatus. Most of the conventional methods for the measurements of creep are limited to below ~1,700 °C. For testing in the range of 1400°C to 1700°C, a thermal gradient design is required to cool the grips. This arrangement requires extremely long specimens which are expensive and time consuming to fabricate and finish. Notable exceptions are measurements of tungsten and its alloys at temperatures up to 2800 °C, using electric resistance heating in the specimen and large thermal gradients. However, these methods are not applicable to nonconductors or to materials which cannot be formed into a wire.

Creep is the time-dependent deformation of a material under constant stress, usually at high temperature. The strain rate $\dot{\varepsilon}$ has been observed to follow the relation $\dot{\varepsilon} = C\sigma^n f(T)$ where $\sigma$ is the stress, $n$ is the stress exponent, $f(T)$ is a function of temperature, and $C$ is a constant. The stress exponent $n$ is determined from multiple measurements at different stresses at the same temperature, with a typical accuracy of many tens of percent in $n$ (Fig. 1.)

Because of the limitations of conventional testing methods, high-temperature creep behavior is often extrapolated from low-temperature measurements. This extrapolation is often inaccurate, especially for multi-phase materials. A new non-contact method for measuring creep of ultra-high-temperature (>2,000 °C) materials is strongly demanded. This method must be to both metallic and nonmetallic materials, for the future technologies of high performance rockets, hypersonic aircraft, and high efficiency energy conversion systems.

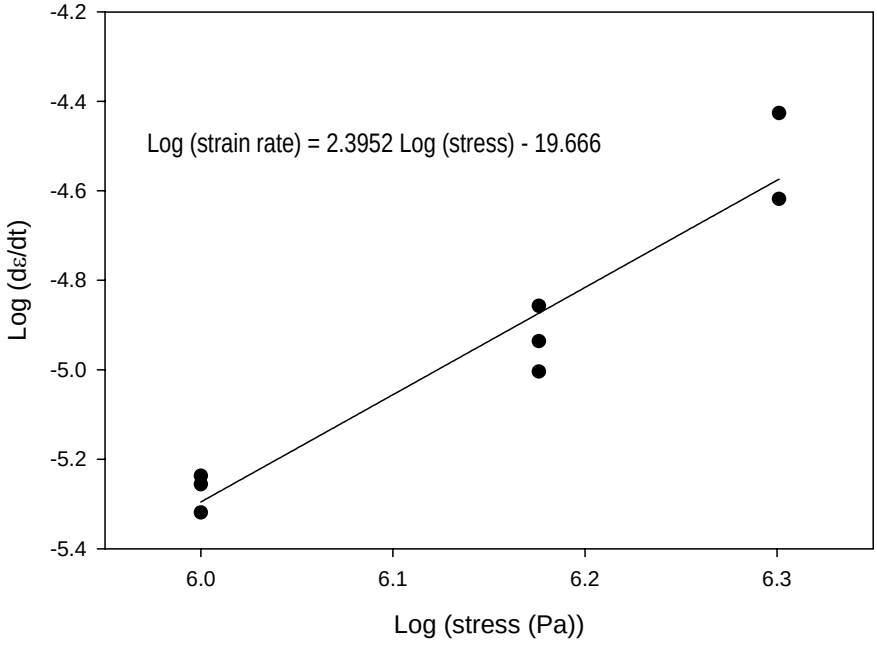


**Figure 1 Strain rate vs. stress for conventional creep measurements, Nb at 1,985 °C under 1.0, 1.5, and 2.0 MPa.**

**3.2 Non-contact creep method**

Our team has developed a novel approach to measuring creep at extremely high temperatures using electrostatic levitation. This method has been demonstrated to measure creep of niobium up to 2300°C [4], while ESL has melted tungsten (3400°C) [5]. The small samples used in this method, 2-3 mm diameter spheres, allow a significant advantage in material utilization and cost of fabricating samples.

The basis of this method is that a rotating sphere experiences a shear stress $\tau$ that is determined by its angular velocity $\omega$, radius $R$, and density $\rho$. The maximum shear stress is $\tau_{\max} = 0.211\omega^2 R^2 \rho$. The sample then creeps under the applied load. For $ZrB_2$ rotating at 4000 Hz (240,000 RPM), the shear stress developed at the center is approximately 1 MPa.

Achieving such high rotation rates is challenging, but not impossible. Since the ESL samples are heated by a laser, we have used photon pressure to accelerate the samples. Each absorbed photon transfers its momentum to the sample. The heating laser is aligned off the axis of the sample, so that this momentum transfer results in a net torque. For 2.2 mm diameter $ZrB_2$ spheres at 2200°C, using the properties in references [7,8] gives an estimate of about 45 minutes to reach the 4000 Hz required for 1 MPa stress. 10 MPa is predicted to require 12,650 Hz and just over 2 hours of acceleration. For comparison, our experiments achieving just less than 1 MPa in niobium required about 3000 Hz rotation.

Since summer 2009, most experiments have been conducted using an induction motor to cause the rotation of the samples instead of photon pressure. The induction motor decouples load from temperature, allowing higher stresses at lower temperatures, but is limited to conducting samples.

As the sample deforms, its surface shape is captured by high-speed video (Figs. 2-3). The shape at each time is measured by a high-precision machine vision algorithm developed at the University of Massachusetts [9]. This method can determine the surface shape to approximately 170 parts per million (ppm), or approximately 190 nm [10]. The deformations are compared to finite element models to determine the constitutive constants in the creep relation. Furthermore, the shape of the surface is uniquely determined by the stress exponent. With our method, the stress exponent can be determined to an accuracy of a few percent and with a single test. This accuracy compares favorably with the many tens of percent typical of conventional methods, which also require many tests at different stress levels to determine the stress exponent.

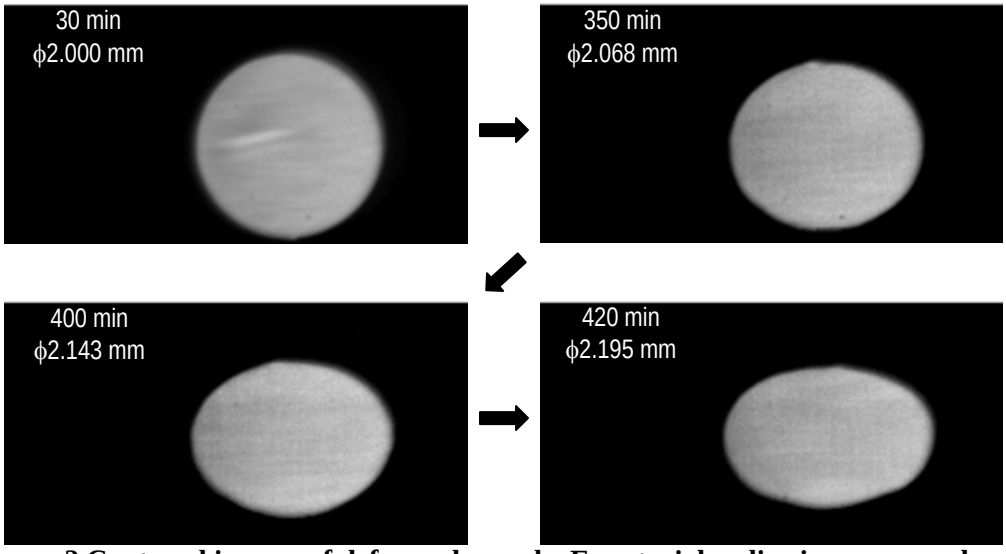


**Figure 2 Captured images of deformed sample. Equatorial radius increases and polar radius decreases as the deformation proceeds.**

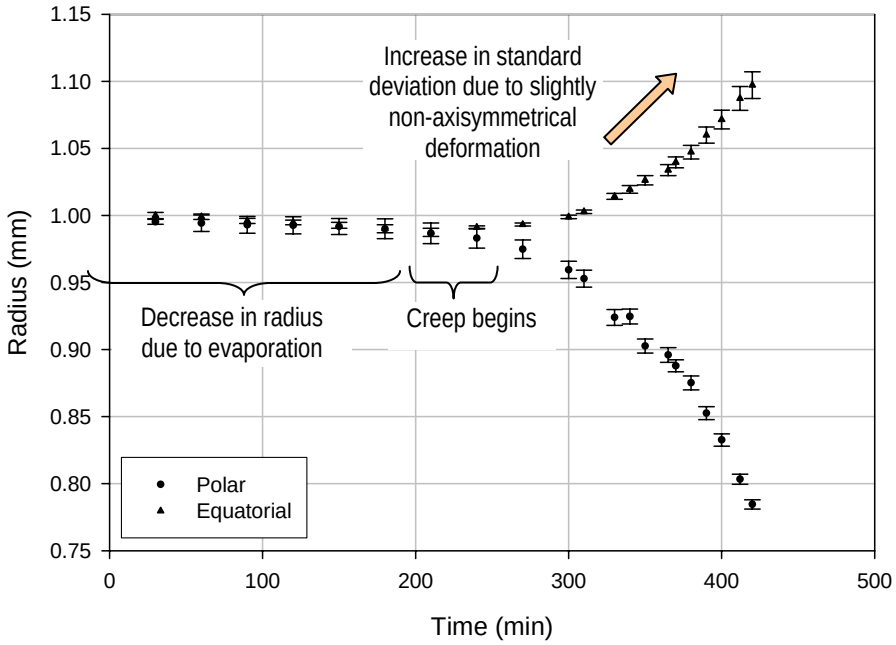


**Figure 3 Plot of the change both polar and equatorial radii of the sample. In the beginning, the equatorial radius decreases due to the mass evaporation.**

Our non-contact method was validated in collaboration with the University of Tennessee for niobium at 1985 °C. Through the heroic efforts of our contractor, Pittsburgh Materials Testing, Inc., conventional tests were completed at this temperature. Conventional tests at 2000ºC were unsuccessful due to a reaction between the sample and the grips. Comparison with conventional experiments showed agreement within the uncertainty of the conventional measurements.

**Table 1 Stress exponent of Nb at 1985ºC**

| | |
|---|---|
| **ESL, UMass/NASA, 2006** | **2.52±0.02** |
| **Conventional Test, UT, 2006** | **2.4 ±1** |
| **Kiessig & Essmann, [11] 1985** | **2.476 ±?** |
| **Frost & Ashby, [12] 1982** | **4.4 ±?** |

### 3.3 Organization and Project Management

The project is a collaboration among Dr. Robert W. Hyers (RHA, PI), Dr. Jan R. Rogers (NASA, co-I), and Prof. Mario Rotea (UMass, co-I). RHA managed the overall project and is responsible for delivery of the deliverables proposed. NASA provided ESL processing and development of processing techniques in accordance with the subaward. UMass provided data reduction and analysis and finite element modeling in accordance with the subaward. Other personnel involved in the project were project manager Liz Hyers, RHA; graduate students Stacy Canepari and Xiao Ye, UMass; and ESL staff Trudy Allen and Glenn Fountain at NASA.

**3.4 Task 1: Process UHTC materials at the relevant temperatures in Electrostatic Levitation for extended periods.**

Preliminary work on this task had been performed in September 2006 at the NASA MSFC ESL by Dr. Jan Rogers, Tom Rathz, and Trudy Allen. Pure $ZrB_2$ material was donated by Dr. Eric Wuchina of the NSWCCD. The NSWCCD provided more $ZrB_2$ and $ZrB_2$-SiC composite material for the current effort.

In 2006, a hand-filed spheroid of this material was processed in ESL at up to 2500°C, heated by a carbon dioxide laser (10.6 micron wavelength). The temperature was measured by pyrometry, and the relevant spectral emissivities were recorded by the ESL team. The sample showed an insignificant mass loss of approximately 0.5%. Residual gas analysis detected strong peaks of Helium, consistent with the processing of the sample material. No special handling was required. The samples were held over 1950°C for a total of approximately one hour. Additional processing in the spring of 2009 confirmed the processability of low-precision samples of this material.

Task 1 was completed successfully: processing of $ZrB_2$ in ESL at temperatures over 2200°C has been demonstrated.

**3.5 Task 2: Prepare the required high-precision spheres from UHTC materials.**

RHA subcontracted the task of grinding the spherical samples to of Industrial Tectonics, Inc. (ITI) of Dexter, MI (www.itiball.com). The NASA ESL and UMass groups have employed ITI's services for fabrication of high-precision spheres for many years. The 4 weeks estimated in the proposal for sample fabrication in the proposal proved too optimistic; in contrast to our prior experience, negotiation of the subcontract alone took that long. ITI experienced several issues with sample fabrication, related to roundness and surface finish of the spheres. In the end, ITI was able to manufacture ball grade 25 spheres, with a sphericity of 25 microinches (~635 nm), but not until after the period of performance of this Phase I project had expired. Experience now indicates that six months should be allowed for fabrication of samples from materials like $ZrB_2$. RHA has also identified a potential second source, PremaTech Advanced Ceramics in Worcester, MA, who may also be able to manufacture high-precision spheres for future experiments.

Task 2 was completed successfully: high-precision samples were successfully fabricated.

**3.6 Task 3: Apply sufficient rotation in the sample to cause creep.**

The preliminary estimates given in the proposal in February 2008 were based on a stress of 1 MPa, corresponding to a rotation rate just under 4000 Hz. The flexural creep measurements of Talmy, *et al.*, [6], published in May 2008, show that much higher stresses are required to get the required deformation within a reasonable experiment duration. Finite element calculations by our research institution, UMass, confirm that a rotation rate closer to 32,000 Hz is required to provide the 100 MPa of stress required to get strain rates of the order of $10^{-5}$/sec to allow the sample to deform ~9% within a 1-day test [13] (attached as Appendix). At this rotation rate, sufficient deformation is predicted for temperatures exceeding 1800°C for pure $ZrB_2$, and 1500°C for $ZrB_2$ + 25 vol% SiC. The lower density of the composite does cause a lower stress at the same rotation rate, but this lower stress is more than compensated for by the faster creep of the composite.

Meanwhile, a magnetic device for inducing sample rotation was developed under separate support through NASA's Innovative Partnerships Program. This new method uses a rotating magnetic field to induce a torque in electrically conducting samples. It was demonstrated successfully on low-precision $ZrB_2$ spheres up to 4000 Hz in July 2009, limited by problems related to the shape of these low-precision samples. The magnetic rotation device has since been demonstrated to cause rotation rates over 13,000 Hz on high-precision spheres of other materials. The hardware was designed to induce rotation at rates up to and exceeding the 32,000 Hz indicated by the finite element simulations.

Coupled with the latest measurements, simulations show that rotation rates near 32,000 Hz are required to a cause sufficient creep rate to complete the experiment in one day. The electromagnetic induction motor was designed to provide rotation rates this high. Experiments show that the

electromagnetic induction motor couples well to the $ZrB_2$ samples. These factors indicate that creep measurements using this method are feasible in ESL, even though the integrated demonstration of creep originally planned was delayed past the end of the period of performance by the problems with sample manufacture.

### 3.7 Task 4: Measure the creep deformation with sufficient precision and accuracy.

In measuring the creep deformation, a few requirements must be met. First, the sample must deform axisymmetrically. Accordingly, the samples must start axisymmetric, so high-precision spheres are used for these measurements. Achieving symmetrical deformation also requires that the samples be either single crystals or fine polycrystals. The materials received from the NSWCCD are of the latter category; with approximately 200 grains spanning the sample diameter, they are expected to deform isotropically.

Second, the video technique must be able to determine the surface shape very precisely. We estimate the surface was determined to approximately 170 parts per million (ppm), or approximately 190 nm. Such accuracy is necessary to allow determination of the stress exponent to an accuracy of a few percent from a single test. Besides axisymmetry, the sample must also have a smooth surface and provide sufficient contrast for imaging the surface with the high-speed camera. The smooth surface is provided by the grinding operations by ITI. At the target measurement temperatures, the samples are sufficiently self-illuminated to provide good contrast as well. The video imagery will be acquired with NASA ESL's Phantom V7 high-speed digital camera. The use of this camera is included with the use of their facility.

Successful completion of this task required high-precision spheres that were not available within the period of performance of this project.

### 3.8 Task 5: Extract the constants in the creep constitutive equation.

This task involves running finite element simulations of the deformation of hypothetical samples under the load history experienced by the actual sample, and using those results to determine the parameters in the constitutive equation for creep that best match the response of the actual sample. This task was intended to be applied to the results of Task 4. Lacking those results, the simulations were instead performed using the same finite element models to predict the performance under different ideal experimental conditions. These results are summarized in section 3.6, above, and reported in detail in [13].

The feasibility of this task had been established on Nb samples prior to the Phase I work, and was demonstrated in simulation during the Phase I project.

### 3.9 Task 6: Compare results to the values reported in the literature and report.

The results of the simulations were presented at the AFOSR Workshop on Materials for Extreme Environments, August 3-5, 2009, and submitted to the Journal of the European Ceramic Society [13]. These simulations show that we can expect to compare directly to the highest temperature measured by Talmy, *et al.*, [6] for the composite, but that we can only compare to extrapolations of their results for the pure $ZrB_2$. The preliminary experiments with low-precision spheres were also presented at the workshop.

## 4 SUMMARY AND CONCLUSION

A 9-month study of the feasibility of applying the non-contact technique for creep measurement to $ZrB_2$ and $ZrB_2$ + SiC composites was carried out. Processing of low-precision samples shows that these materials may be processed in ESL at temperatures over 2000°C, and up to 2500°C for the pure material. The composite shows a eutectic at 2270°C, and so should not be processed too close to this temperature. The materials couple well with the new electromagnetic rotator, allowing much higher stresses as well as expanding the time under load that may be accomplished in the experiments. Finite element simulations were performed with parameters extrapolated from reported measurements of the creep of $ZrB_2$ and $ZrB_2$ + SiC composites. These simulations indicate that the experiments are feasible

within the designed performance of the electromagnetic rotator within the allotted experiment duration. High-precision samples of ball grade 25 were successfully fabricated of both materials, $ZrB_2$ and $ZrB_2$ + 25 vol% SiC. These factors combine to provide a strongly positive indication of the feasibility of applying this method to these ultra-high-temperature materials.

A series of delays, including a time to manufacture the samples that was 5 months longer than projected, meant that the final integrated test with high-precision spheres could not be completed within the period of performance of the contract.

## 5 ACKNOWLEDGMENT

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## APPENDIX: MANUSCRIPT DESCRIBING SIMULATION METHODOLOGY AND RESULTS

The following manuscript is reference [13], which was submitted in September 2009 for review by the Journal of the European Ceramic Society.

# Computational Methods for the Analysis of Non-contact Creep Deformation in $ZrB_2$-SiC Composites

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**Abstract:**

A need for higher service temperatures is driving development of new, higher-temperature materials that are resistant to creep. However, conventional methods of measuring creep become increasingly difficult over about 1700°C. A non-contact method with the capability of measurements at much higher temperature has been demonstrated on niobium using centrifugal loading of a spherical sample. Recent efforts have been made to extend this method to lower temperatures and higher stresses. Using material properties from the literature, we performed finite element simulations to determine the range of experimental parameters over which non-contact measurements of creep can be readily finished within a reasonable time duration for $ZrB_2$ and $ZrB_2$ + 25 vol% SiC. Results from FEA model shows that the experiments are feasible at an angular velocity of 32,000 rps and a temperature as low as 1800 °C for $ZrB_2$ and 1500 °C for $ZrB_2$ + 25 vol% SiC.

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*Keywords:* Creep, Borides, Composites, Ultra high temperature ceramics.

## 1. Introduction

Modern applications such as rocket nozzles, leading edges of hypersonic airplanes, and next generation turbine blades place demanding requirements on ultra-high temperature ceramics. Besides requirements for general mechanical strength and oxidation resistance, at high temperature, creep resistance is one of the most crucial criteria. UHTCs, including transition metal carbides, oxides and borides are of current interest for these applications. Zirconium diboride ($ZrB_2$) is characterized by a high melting point (3040°C), high hardness (22 GPa) and good corrosion resistance due to its high percentage of covalent bonding.[1] However, at temperature greater than 650 °C, its resistance to chemical attack by oxidation is not satisfactory to accommodate atmospheric applications. In order to improve its oxidation resistance at elevated temperature, different additions have been introduced. Among them, 25 vol% SiC is currently the most promising for applications in oxidizing environments.[2]

### *1.1 Fundamental creep behavior*

Creep is defined as a time-independent deformation that usually should be included into consideration when using a material in conditions like this: temperature higher than half of its absolute melting point and subjecting to a stress load lower than its yielding point. The rate of creep is affected by various factors, such as material properties, exposure temperature, exposure time and applied stress. Despite the differences between various creep mechanisms, a complete creep behavior generally can be divided into three

stages based on their different creep rate characteristics. In stage 1, (transient creep), the creep rate decreases until a minimum steady-state is reached, which is stage 2. Transmission-microscopic examination shows that at the beginning stage material structure evolves with a significant strain accumulation, which corresponds to a dramatically dislocation density rise. And then during the following stage, speed of new dislocation generation and annihilation among dislocation balance to each other to reach a steady state macroscopically. In stage 3, creep rate rise again until fracture happens.

*1.2 Non-contact measurement of creep*

Since creep resistance is an important criterion in demanding applications, accurate measurement of creep behavior of candidate materials will be required. At high temperature, materials are highly reactive. Reaction with the test fixtures generally excludes conventional method for measuring creep above about 1700 °C. A group in UMASS has been working on non-contact measurement of creep behavior since 2004. Lee *et al*.[3], used Electrostatic Levitation (ESL) to levitate spherical Nb specimen under high vacuum ($\approx 10^{-7}$ torr) at NASA Marshall Space Flight Center (MSFC) in Huntsville, AL. This apparatus has a demonstrated capability to process samples at extremely high temperatures, having been used to melt tungsten (3410 °C).[4]

Specimens were stabilized via three pairs of orthogonal electrodes controlled by PID control-loop. A 200 W YAG laser beam was cast on the sphere to heat and rotate the sample. The shape of the spherical sample was captured with a digital camera and the captured images were analyzed to determine the amount of deformation of the sample. Meanwhile an ANSYS model was established to simulate creep behavior of the sphere

with different stress exponent at the same conditions as real experiment. By comparing the deformed shape of the sample to the ANSYS model, the stress exponent of the specimen can be determined, which further helps in determine the creep mechanism. The stress exponent measured in this way agrees with conventional tensile measurement.

In this paper, based on the same idea, creep data for $ZrB_2$ and $ZrB_2$ + 25 vol% SiC was collected by screening available literature and input into the model. Ideal simulation results will help evaluate the feasibility of using this technique for UHTC's and to plan the experimental matrix.

*1.3 Experimentally determined creep behavior in UHTCs*

I. G. Talmy *et al*.[5] characterized flexural creep of $ZrB_2$ + 0-50 vol% SiC as a function of temperature (1200-1500 °C), stress (30-180 MPa) and SiC particle size (2 and 10 $\mu m$) in ambient air via four-point flexural creep test. Specimens were synthesized by hot pressing commercially available $ZrB_2$ and SiC power at 2100 °C for 1 h with 20 MPa pressure in He atmosphere. The creep rate increased with increasing SiC content, temperature, and stress and with decreasing SiC particle size, especially, at temperatures above 1300 °C. The activation energy of creep turned out to be a function of SiC content and increased linearly with it for ceramics containing 0-50 vol% 2 $\mu m$ SiC. At 1400 °C, the reported stress exponent was 1.1 for Pure $ZrB_2$ and 0.7 for $ZrB_2$/25 vol% 2 $\mu m$ SiC respectively, which indicated for both compositions diffusional creep had a great contribution to total creep deformation at these temperatures. Cracking and grain shifting were observed on the tensile side of 25 vol% SiC specimen. Also, the presence of stress, both compressive and tensile, promoted oxidation.

Melendez-Martinez *et al*.[6] evaluated creep behavior of pure $ZrB_2$ and $ZrB_2$ + 4 wt% Ni at temperatures between 1400 and 1600 °C and at stresses ranging from 47.0 to 472.3 MPa for pure $ZrB_2$ and 10 to 63.5 MPa for Ni-doped $ZrB_2$. The compressive creep test was performed in controlled argon atmosphere via a prototype dead-weight load device on specimens which were hot pressed at 1900 °C (pure $ZrB_2$) and 1850 °C (Ni-doped $ZrB_2$) for 30 min with applied pressure of 30MPa. The following mechanical properties were measured: elastic modulus (E) by the resonance frequency method, flexural strength (S) by four-point flexure test, microhardness (Hv1.0) by a Vickers indenter. Pure $ZrB_2$ showed only little creep deformation at temperature below 1400 °C and stress below 298MPa. The reported stress exponent was 1.7 at 1500°C and 0.6 at 1600°C below 220MPa. The Ni-doped $ZrB_2$ failed catastrophically for stress high than 25MPa and shows a ductile behavior only at lower stress. The stress exponent was 1.5 at 1500 °C and stress between 10 and 20 MPa. This behavior may be attributed to the presence of Ni-rich grain boundary phases at triple points of the grain structure.

## 2. Procedure

A sphere model with radius 1.1mm was established in ANSYS. Creep behavior of two different materials was simulated with ANSYS: Pure $ZrB_2$ and $ZrB_2$ + 25 vol% SiC.

An implicit creep equation was chose to model the creep behavior of the sphere. Values for parameters used in this equation were collected by surveying the literature. Some of them were well known or could be easily extrapolated from available data, such as density ( $\rho$ ), Young's modulus (E), Poisson's ratio ( $\upsilon$ ), others were extrapolated from existing data. Since the purpose of this model is to evaluate feasible range for

experiments, and the uncertainty involved in these extrapolations is acceptable in the absence of previous measurements. These material properties were input into the finite element model of the rotating sample. The model was run for various conditions to determine the range of experimental parameters that is expected to provide sufficient creep deformation within the duration of experiment.

*2.1 Mechanical properties*

Recently, $ZrB_2$ and $ZrB_2$-based composites have been densified by various methods, including hot pressing, reactive hot pressing, plasma sintering and pressureless sintering. Slight changes in processing conditions, such as temperature, thermal history, hold time, pressure, or species and quantities of additives will all have reflections in product's mechanical properties.

Chamberlain *et al*.[7] densified $ZrB_2$ and $ZrB_2$ ceramics containing 10, 20 and 30 vol% SiC particulates from commercially available powders by hot pressing and measured density, four-point bend strength, fracture toughness, elastic modulus and hardness at room temperature. The data for $ZrB_2$ + 25 vol% SiC, can be interpolated by taking arithmetic mean of the same properties of materials with close composition. Table 1 shows the data for $ZrB_2$ and $ZrB_2$ + 25 vol% SiC at room temperature.

At high temperature, it is hard to measure properties like Young's modulus. There are only limited data of mechanical properties concerning transition metal borides. Opeka *et al*.[2] measured mechanical properties for $HfB_2$, $HfC_{0.98}$, $HfC_{0.67}$, and $HfN_{0.92}$ ceramics. They reported that all these ceramics will experience a dramatic modulus loss beginning as low as 1090 °C. $HfB_2$ lost about 75% of its room temperature modulus at 1640 °C.

Accordingly, in order to account for this modulus loss, a Young's modulus of 120 GPa was used for pure $ZrB_2$ and 130 GPa for $ZrB_2$ + 25 vol% SiC for all the temperatures considered in our simulation. Since Young's modulus would have a considerable impact on only the elastic deformation of specimen sphere, which is much smaller than the creep deformation (plastic deformation), the accuracy of this estimation should be sufficient.

Another mechanical property required for ANSYS model is Poisson's ratio. In contrast to other properties, it is insensitive to additives as well as to porosity caused by different processing conditions. It remains almost constant for various $ZrB_2$-based composites.[8-10] Guo *et al*. measured mechanical properties for ten different series of hot pressed $ZrB_2$-$MoSi_2$-SiC, ranging from 10 to 40 vol% for $MoSi_2$, and 5 to 20 vol% for SiC, at 1800 °C for 30 min under a pressure of 20MPa in vacuum. Poisson's ratio barely changes for these different materials. Table 2 shows Poisson's ratio for pure $ZrB_2$ and $ZrB_2$ + 25 vol% SiC we used in all simulations. Small changes due to differences from the reference temperature will be neglected.

*2.2 Creep model and determination of its parameters*

As a powerful and widely used Finite Element Analysis (FEA) software package, ANSYS was used to simulate creep behavior of monolithic $ZrB_2$ and $ZrB_2$ + 25 vol% SiC. ANSYS provides as much as 13 featured implicit creep models to simulate primary and secondary creep behavior. The Norton model (eq.1) was chosen for these simulations due to its programming-friendly concise expression:

$$\dot{\varepsilon} = C\sigma^n e^{\left(-\frac{Q}{KT}\right)} \qquad (1)$$

where $\dot{\varepsilon}$ is the strain rate, coefficient C is a material constant, n is the stress exponent, Q is the activation energy, and R is the universal gas constant, which equals $8.314 J/mol \cdot K$. The stress exponent is determined by the creep mechanism, which is itself dependent on temperature. For diffusional creep usually dominant at low stress, such as Coble creep and Nabarro-Herring creep, n is close to 1, while for power law creep, which usually happens at high stress, n is greater than 1. The thermal activation energy, in contrast, is insensitive to creep mechanism but depends mainly on material's composition. The thermally activated nature of creep implies a strong dependence on temperature of the strain rate.

I. G. Talmy *et al*.[5] reported that stress exponent was about 1 for $ZrB_2$ containing 0-25 vol% SiC around 1400 °C, which indicated that diffusional creep was the dominant creep mechanism. The activation energy didn't change within test temperature ranging from 1200 °C to 1500 °C for $ZrB_2$-based composites of varying SiC content: $130 kJ/mole$ for pure $ZrB_2$ and $276 kJ/mole$ for $ZrB_2$.+ 25 vol% SiC. The leading coefficient C can be calculated using equation (1), which yields $3.965\times10^{-13}/\sec$ for pure $ZrB_2$ and $2.084\times10^{-4}/\sec$ for $ZrB_2$.+ 25 vol% SiC.

Lee *et al*.[3] used the same creep model for simulating niobium (Nb) sphere's creep behavior. Angular velocity was set to be 20106 rad/s (3200 rps) to apply a shear stress load about 1MPa at sphere center. They reported a 3300s predicted duration of experiment to reach the stop criterion of 9% equatorial creep deformation, which was the same as we used here. The creep rate was at the order of $10^{-5} s^{-1}$.

The maximum shear stress in the sample varies with sample size and rotation rate according,

$$\tau = 0.211\omega^2 r^2 \rho \qquad (2)$$

where $\omega$ is angular velocity (rad/s), r is radius of the sphere, $\rho$ is material density.

Achieving stresses similar to those reported by Talmy *et al*.,[3] requires an angular velocity of 201060 rad/s (32,000rps).

However, the creep rate reported by Talmy *et al*. at 1400 °C and 100MPa pressure is only $10^{-8} s^{-1}$ for pure $ZrB_2$ and $10^{-7} s^{-1}$ for $ZrB_2$ + 25 vol% SiC, respectively, both of which are too small to reach a satisfactory strain of 9% equatorial deformation within a few hours. Increasing temperature is necessary to have a creep rate comparable to Lee's. Extrapolation of Talmy's data gives 1800 °C for pure $ZrB_2$ and 1500 °C for $ZrB_2$ + 25 vol% SiC. The corresponding stress exponent and resulting coefficient C from equation (1) are given in table 3.

## 3. Result and discussion

For every 1000 simulation seconds before 94% of desired strain and later on 10 simulation seconds, angular velocity was updated to account for changes in polar moment of inertia which resulted from shape change. The simulation runs about 3 hours for pure $ZrB_2$ and 5 hours for $ZrB_2$ + 25 vol% SiC in an Intel core 2 computer.

For pure $ZrB_2$, the model shows that the equatorial and polar radii are $1.199\times10^{-3} m$ and $9.287\times10^{-4} m$, respectively, which corresponds to 9% strain at the equator after an elapsed time of 5102 seconds. The deformation in the x direction of the XZ plane and von Mises stress contour are plotted in Figures 1 and 2, respectively.

For $ZrB_2$ + 25 vol% SiC, model showed that the equatorial and polar radii are $1.199\times10^{-3}m$ and $9.164\times10^{-4}m$, respectively, at run time 12272 sec. X direction deformation & von Mises stress contour are showed in Figures 3 and 4.

The simulations show that completing experiments with an 8-hour shift is feasible, if only at very high angular velocity around 32,000 rps. Although the method has been demonstrated only at speeds up to 11,000 rps, work is underway at UMASS and NASA to extend the experimental range to speeds over 30,000 rps. The results of the simulations here show the importance of this capability for higher speeds to enable the high loads needed for testing creep in UHTC's in a short-duration experiment. With the extended range of rotational speed and stress, the range of applicability of the new method overlaps with conventional methods, while still providing the capability of measurements at much higher temperatures than conventional methods.

## 4. Summary

A sphere model was established in ANSYS. Rotating at an angular velocity of 201060rad/s (32,000rps), the sphere was subjected to a maximum shear stress about 100MPa at its center. Due to its programming-friendly concise expression, the Norton model was used to depict this creep behavior. From available literature, parameters in Norton model at 1400 °C were calculated for $ZrB_2$ and $ZrB_2$ + 25 vol% SiC, which functioned as a reference point for approximating same parameter at adjacent temperature.

In order to get a 9% equatorial deformation within several hours, the strain rate should be at the order of $10^{-5}$ / sec which is comparable to our group's previous work. Achieving this fast creep rate requires a temperature of 1800 °C for $ZrB_2$ and 1500 °C for $ZrB_2$ + SiC, even at angular velocity as high as 32,000 rps. The simulation results agree quite well with what we expected and previous work. The simulations also show that this very high angular velocity is necessary to complete the measurements with the feasible time on the NASA ESL, showing the importance of this new experimental capability.

## 5. Acknowledgement

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## 7. Figure captions:

Fig.1. X direction deformation profile of XZ plane for pure $ZrB_2$. Generally, material subjects to increasing shear force proportional to its distance to the sphere center.

Fig.2. Von Mises stress plot of deformed pure $ZrB_2$. According to equation (2), Shear force scales with square of its distance to the sphere center. This plot agrees with theoretical prediction.

Fig.3. X direction deformation profile of XZ plane for $ZrB_2$ + 25 vol% SiC. Material subjects to increasing shear force proportional to its distance to the sphere center.

Fig.4. Von Mises stress plot of deformed $ZrB_2$ + 25 vol% SiC. According to equation (2), Shear force scales with square of its distance to the sphere center. This plot agrees with theoretical prediction.

## 8. Tables:

**Table 1**. Density and Young's modulus for pure $ZrB_2$ and $ZrB_2$ + 25 vol% SiC at room temperature. Read data for $ZrB_2$ and interpolate data for $ZrB_2$ + 25 vol% SiC from materials with close composition based on Chamberlain *et al.'s*[5] work.

| Material | Density ( $g / cm^3$ ) | Young's modulus (GPa) |
|---|---|---|
| Pure $ZrB_2$ | 6.26 | 489 |
| $ZrB_2$ + 25 vol. % SiC | $5.60^*$ | $475^*$ |

Data with superscript * means interpolated data.

**Table 2**. Poisson's ratio for pure $ZrB_2$ and $ZrB_2$ + 25 vol% SiC. Since Poisson's ratio is almost insensitive to additives and processing conditions, we assume that Poisson's ratio is constant over interested temperature span of our simulations.

| Material | Poisson's ratio |
|---|---|
| Pure $ZrB_2$ | 0.15 |
| $ZrB_2$ + 25 vol% SiC | 0.15 |

**Table 3**.

Parameters of Norton creep model for $ZrB_2$ and $ZrB_2$ + 25 vol% SiC as well as estimated stress rate.

| Material | Temperature(°C) | Stress exponent | Coefficent($s^{-1}$) | Estimated Creep rate ($s^{-1}$) |
|---|---|---|---|---|
| Pure $ZrB_2$ | 1800 | 3 | $1\times10^{-25}$ | $1.4305*10^{-5}$ |
| $ZrB_2$ + 25 vol% SiC | 1500 | 1.3 | $1\times10^{-7}$ | $9.1212\times10^{-6}$ |

**Figure**

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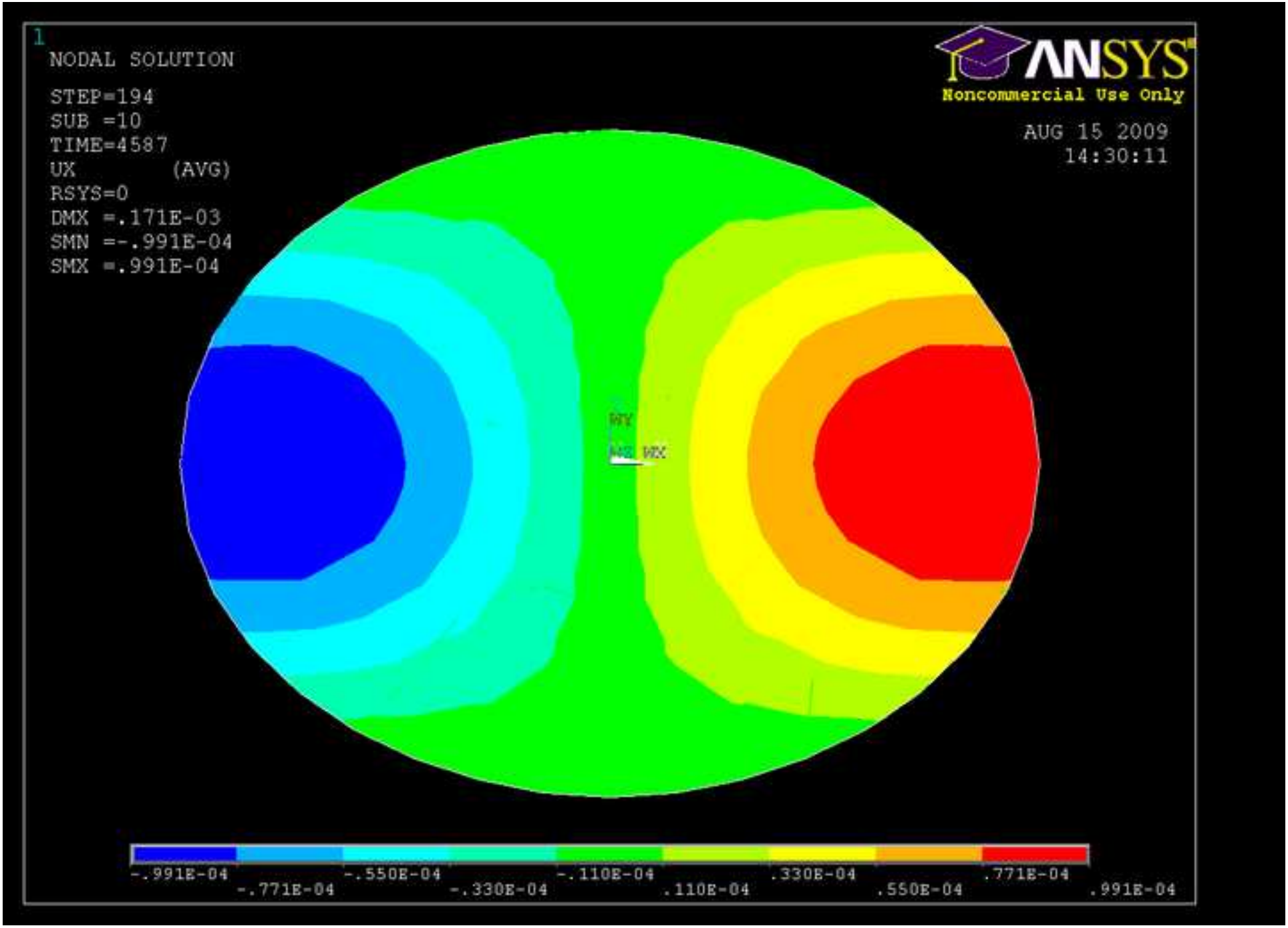

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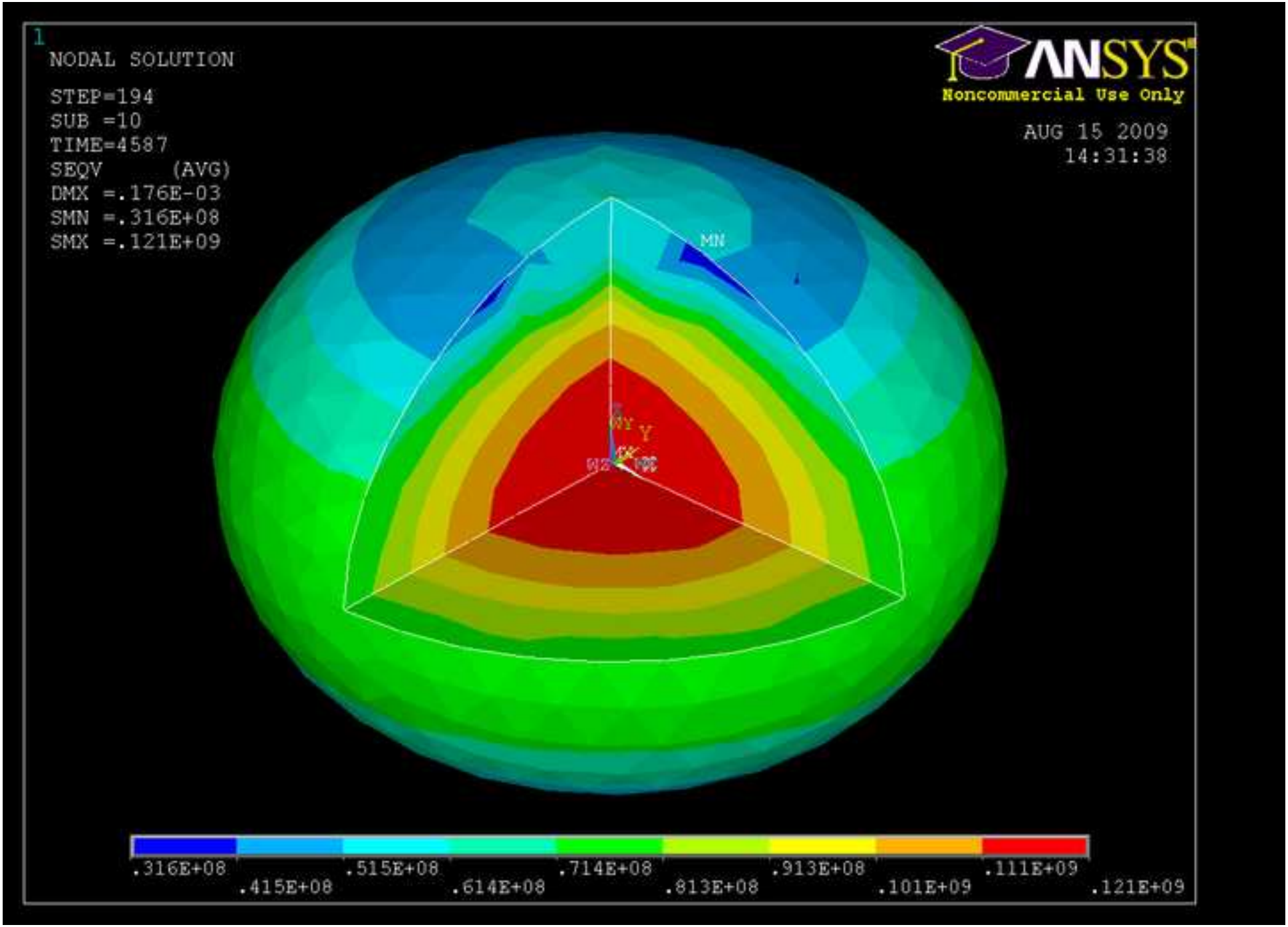

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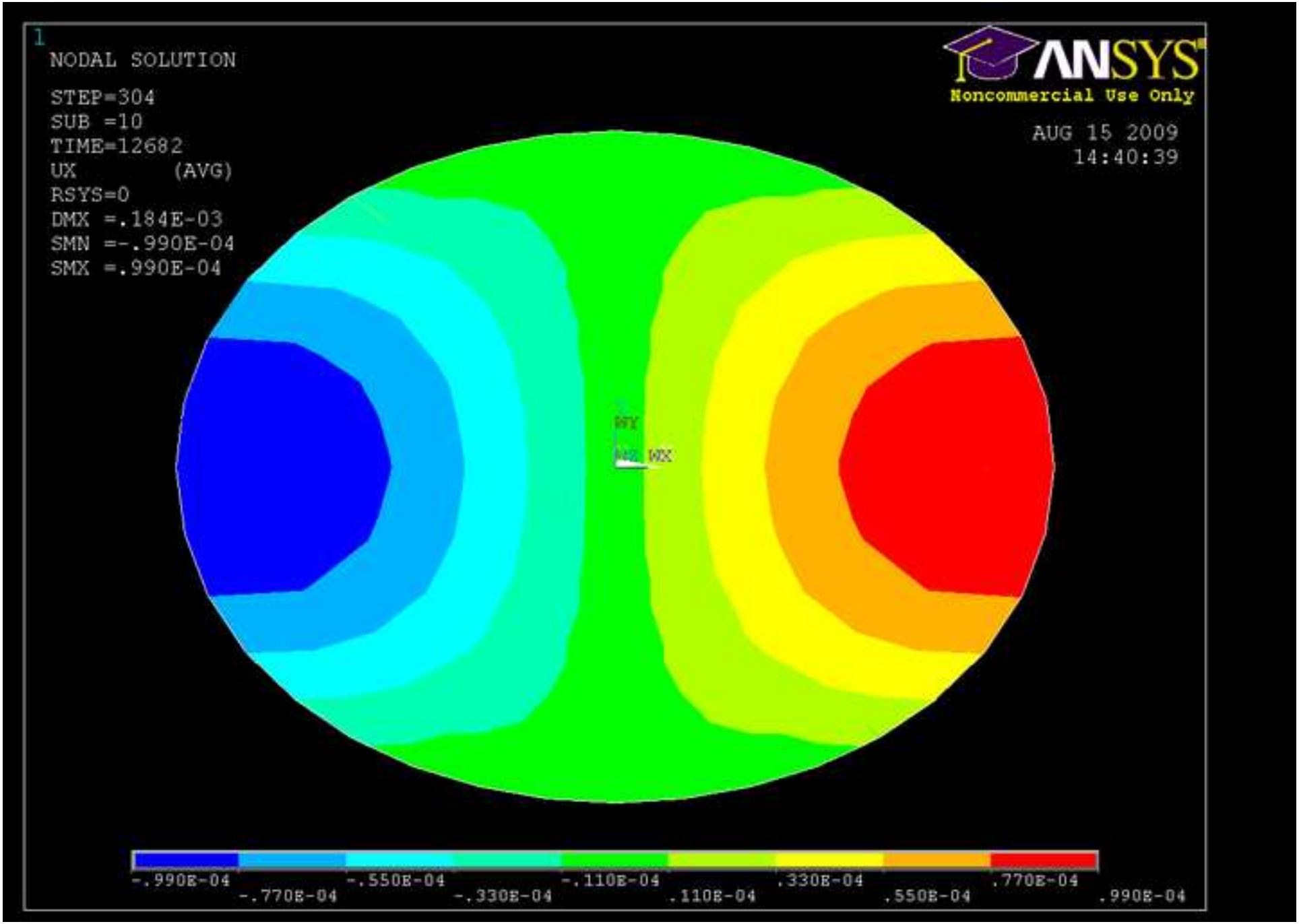

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